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Influence of Blending Canola, Palm, Soybean, and Sunflower Oil Methyl Esters on Fuel Properties of Biodiesel[†]

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Single, binary, ternary, and quaternary mixtures of canola (low erucic acid rapeseed), palm, soybean, and sunflower (high oleic acid) oil methyl esters (CME, PME, SME, and SFME, respectively) were prepared, and important fuel properties were measured, such as oil stability index (OSI), cold filter plugging point (CFPP), cloud point (CP), pour point (PP), kinematic viscosity (40 °C), lubricity, acid value (AV), and iodine value (IV). The fuel properties of SME were improved through blending with CME, PME, and SFME to satisfy the IV (<120) and OSI (>6 h) specifications contained within EN 14214, the biodiesel standard from the European Committee for Standardization. SME was satisfactory according to ASTM D6751, the American biodiesel standard, with regard to OSI (>3 h). The CFPP of PME was improved by up to 15 °C through blending with CME. Statistically significant relationships were elucidated between OSI and IV, OSI and saturated fatty acid methyl ester (SFAME) content, OSI and CFPP, CFPP and IV, and CFPP and SFAME content. However, the only relationship of practical significance was that of CFPP versus SFAME content when SFAME content was greater than 12 wt %.

1. Introduction

Biodiesel (BD), an alternative fuel composed of monoalkyl esters of long-chain fatty acids prepared from vegetable oils or animal fats, has attracted considerable interest as a substitute or blend component for ultra-low sulfur diesel fuel (ULSD, <15 ppm S). BD possesses significant technical advantages over ULSD, such as inherent lubricity, low toxicity, derivation from a renewable and domestic feedstock, superior flash point, and biodegradability, as well as an overall reduction in most regulated exhaust emissions. Important disadvantages of BD include high feedstock cost, higher regulated NO_x exhaust emissions, inferior storage stability, and low-temperature operability.[1,2] Many of these deficiencies can be mitigated through additives, blending with ULSD, and reducing storage time. However, feedstock cost, which currently accounts for over 85% of BD production expenses, remains a serious threat to the economic viability of the BD industry.[3,4] One solution to this problem is employment of multiple feedstocks of varying type and quality and, hence, cost. Consequently, a portion of BD is the result of mixed feedstock production.[5]

A recent report from the International Grains Council indicated that rapeseed oil was the predominant feedstock for worldwide BD production in 2007 [48%, 4.6 million metric tons (MMT)]. The remaining oils included soybean (22%, 2.1 MMT) and palm (11%, 1.0 MMT), with the rest (19%, 1.8 MMT) distributed among other unspecified vegetable oils and animal fats.[6] According to a recent report by the United States Department of Agriculture (USDA), the leading vegetable oils produced worldwide in 2007−2008 were palm (42.9 MMT), soybean (38.6 MMT), rapeseed (19.0 MMT), and sunflower (11.4 MMT) oils.[7] Correspondingly, BD feedstock usage loosely approximates overall worldwide vegetable oil production.

The fatty ester composition and minor constituent content (tocopherols, tocotrienols, phytosterols, etc.) of BD varies according to feedstock, which in turn influences physical, chemical, and fuel properties.[8] A large number of studies have reported the properties of BD obtained from single feedstock sources, but few have investigated the influence of mixed feedstocks on fuel properties of BD.[9−11] Of these, most report the influence of BD obtained from minor oils on more common BD.[10,11] The objective of this work was to examine the influence of mixing palm, soybean, canola (low erucic acid rapeseed), and sunflower (high oleic acid) oil methyl esters (PME, SME, CME, and SFME, respectively) on important BD fuel properties, such as low-temperature operability, oxidative stability, kinematic viscosity, and iodine value (IV). A comparison with relevant BD standards, such as American Society for Testing

[†] Disclaimer: Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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and Materials (ASTM) D6751[12] in the United States and EN 14214[13] from the European Committee for Standardization (CEN), was also of interest.

2. Experimental Section

2.1. Materials. Refined, bleached, and deodorized (RBD) canola (low erucic acid rapeseed oil), palm, soybean, and sunflower (high oleic acid) oils without commercial additives were purchased from KIC Chemicals, Inc. (New Platz, NY) and used as received. All other chemicals and reagents were obtained from Aldrich Chemical Co. (Milwaukee, WI).

2.2. Transesterification. Methanolysis of triacylglycerols (TAG) was accomplished with a sodium methoxide catalyst (0.5 wt % with respect to TAG), 6:1 mol ratio of methanol/TAG, 60 °C internal reaction temperature, and 1.5 h reaction time. After sequential removal of glycerol by gravity separation and methanol by rotary evaporation, the crude methyl esters were washed with distilled water until a neutral pH was obtained. The ester phase was then dried by washing once with brine solution, followed by treatment with $MgSO_4$ to afford purified and dried fatty acid methyl esters (FAME).

2.3. Mono-, Di-, and Triacylglycerol Content. FAME were checked for mono-, di-, and triacylglycerol content and compared to the retention times of known reference standards using an Agilent (Palo Alto, CA) 6890 GC equipped with an Agilent 6890 series autoinjector. An Agilent DB-5HT column (15.0 m × 320 μm i.d., 6.10 μm film thickness) was used with a He flow rate of 1.9 mL min^{-1}. The temperature program initiated at 50 °C and was held for 1 min, followed by an increase to 230 °C at 7 °C min^{-1}, followed by an increase at 30 °C min^{-1} to 380 °C, which was held for 10 min. The inlet and detector temperatures were set to 320 and 390 °C, respectively. A 2 μL splitless injection volume was used.

2.4. Fatty Ester Profile. FAME were separated using a Varian (Walnut Creek, CA) 8400 GC equipped with a flame ionization detector (FID) and SP2380 (Supelco, Bellefonte, PA) column (30 m × 0.25 mm i.d., 0.20 μm film thickness). The carrier gas was He at 1 mL min^{-1}. The oven temperature was initially held at 150 °C for 15 min and then increased to 210 °C at 2 °C min^{-1}, followed by an increase to 220 °C at 50 °C min^{-1}. The injector and detector temperatures were set at 240 and 270 °C, respectively. FAME peaks were identified by a comparison to the retention times of known reference standards. Each FAME determination was run in triplicate, and average values are reported (Table 1).

2.5. Tocopherol Content. Samples diluted in hexane to a concentration of 50−100 mg mL^{-1} were analyzed by a Varian (Palo Alto, CA) HPLC Pro-Star model 230 pump, model 410 autosampler, and model 363 fluorescence detector. The mobile phase was hexane/2-propanol [99.5:0.5 (v/v), made fresh daily] pumped at a rate of 1 mL min^{-1}. Samples were injected using the full loop option (100 μL), and tocopherols were separated using an Inertsil (Varian) silica column (5 μm, 150 Å, 250 × 4.6 mm i.d.). Tocopherol peaks were identified by a comparison to the retention times of known reference standards. A mixture of α-, β-, γ-, and δ-tocopherol standards was injected on each day of analysis to verify HPLC performance. Samples were quantified using external standard curves. Each determination was run in duplicate (Table 1).

2.6. Properties of Methyl Esters. The cloud point (CP) and pour point (PP) were measured according to ASTM D5773[14] and ASTM D5949,[15] respectively, using a model PSA-70S phase technology analyzer (Richmond, British Columbia, Canada). CP and PP were rounded to the nearest whole degree (°C). For a greater

Table 1. Fatty Ester Composition (wt %) and Tocopherol Content (ppm) of Canola (CME), Palm (PME), Soybean (SME), and Sunflower (SFME) Oil Methyl Esters

	CME	PME	SME	SFME
C12:0		0.3		
C14:0		1.1		
C16:0	4.6	41.9	10.5	4.5
C18:0	2.1	4.6	4.1	4.0
C20:0	0.7	0.3		0.3
C22:0	0.3			1.0
C16:1	0.2	0.2		
C18:1	64.3	41.2	24.1	82.0
C18:2	20.2	10.3	53.6	8.0
C18:3	7.6	0.1	7.7	0.2
Σ SFAME[a]	7.7	48.2	14.6	9.8
Σ UFAME[b]	92.3	51.8	85.4	91.2
α-toco	314	122	62	497
β-toco	18	7	11	21
γ-toco	420	39	537	118
δ-toco	14	6	147	19
Σ toco[c]	766	174	757	655

[a] Σ SFAME = saturated FAME = C12:0 + C14:0 + C16:0 + C18:0 + C20:0 + C22:0. [b] Σ UFAME = unsaturated FAME = C16:1 + C18:1 + C18:2 + C18:3. [c] Σ toco = sum of all tocopherols (α, β, γ, and δ).

degree of accuracy, PP measurements were performed with a resolution of 1 °C instead of the specified 3 °C increment. Cold filter plugging point (CFPP) was determined following ASTM D6371[16] using an ISL automatic CFPP analyzer model FPP 5Gs (Houston, TX). Each experiment was run in triplicate (Tables 2−4).

Kinematic viscosity (ν, mm^2 s^{-1}) was measured with a Cannon−Fenske viscometer (Cannon Instrument Co., State College, PA) at 40 °C in accordance with ASTM D445.[17] All experiments were run in triplicate (Table 2).

Lubricity (lub) was determined at 60 °C (controlled to less than ±1 °C), according to ASTM D6079,[18] using a high-frequency reciprocating rig (HFRR) ball-on-disk lubricity tester (PCS Instruments, London, U.K.) via Lazar Scientific (Granger, IN). Wear scars (μm) from the ball were obtained by measuring the maximum value of the *x* and *y* axes of the scar using a Prior Scientific (Rockland, MA) Epimat model M4000 microscope. The average wear scar diameter was determined by averaging the *x* and *y* axis wear scar lengths. All experiments were run in duplicate (Table 2).

The oil stability index (OSI, h) was measured in accordance with EN 14112,[19] employing a Rancimat model 743 instrument by Metrohm, Ltd. (Herisau, Switzerland). The flow rate of air through 3 ± 0.01 g of sample was 10 L h^{-1}. The block temperature was set to 110 °C, with a correction factor, ΔT, of 1.5 °C. The conductivity measuring vessel contained 50 ± 0.1 mL of distilled water. Each sample was run in triplicate (Tables 2−3).

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Table 2. Fuel Properties of CME, PME, SME, and SFME and Comparison with ASTM D6751 and EN 14214[a]

	ASTM D6751	EN 14214	CME	PME	SME	SFME
CN	47 min	51 min	48−56	62[b]	48−56	54−58
ΔH (kJ kg^{-1})			37300−39870	37400−38320[c]	39720−40080	38100−38472
CP (°C)	report		0 ± 1	17 ± 1	1 ± 1	5 ± 1
PP (°C)			−9 ± 1	15 ± 1	0 ± 1	−2 ± 1
CFPP (°C)		variable[d]	−7 ± 1	12 ± 1	−4 ± 1	2 ± 1
OSI (h)	3 min	6 min	6.4 ± 0.1	10.3 ± 0.1	5.0 ± 0.1	6.2 ± 0.1
v (mm^2 s^{-1})	1.9−6.0	3.5−5.0	4.42 ± 0.23	4.58 ± 0.01	4.12 ± 0.01	4.74 ± 0.01
lub (μm)			169 ± 1	126 ± 1	136 ± 3	152 ± 5
AV (mg of KOH g^{-1})	0.50 max	0.50 max	0.01 ± 0.01	0.01 ± 0.01	0.04 ± 0.01	0.04 ± 0.01
IV		120 max	110	54	134	85

[a] CN, cetane number; ΔH, heat of combustion. CN and ΔH values are from ref 1, except where indicated. [b] From ref 33. [c] From ref 34. [d] Dependent upon the location and time of year.

Table 3. Influence of Mixing Methyl Esters on Biodiesel Fuel Properties

	vol ratio	mixture[a]	OSI (h)	CP[b] (°C)	PP[b] (°C)	CFPP[b] (°C)	IV	SFAME (wt %)
1	1:1	S/C	5.3 ± 0.1	0	−3	−7	121	11.5
2	1:3	S/C	5.9 ± 0.1	0	−5	−8	116	9.6
3	3:1	S/C	5.1 ± 0.2	0	−1	−5	128	13.1
4	1:1	S/P	6.2 ± 0.2	9	8	5	95	30.9
5	1:3	S/P	7.7 ± 0.2	12	13	9	73	40.9
6	3:1	S/P	5.5 ± 0.1	5	4	0	114	22.7
7	1:1	S/SF	5.8 ± 0.1	3	1	−3	109	12.4
8	1:3	S/SF	6.4 ± 0.1	3	−1	0	97	11.1
9	3:1	S/SF	5.4 ± 0.1	2	0	−4	121	13.8
10	1:1	C/P	7.6 ± 0.1	7	6	4	81	27.8
11	1:3	C/P	9.6 ± 0.1	11	12	8	68	38.0
12	3:1	C/P	6.5 ± 0.1	1	0	−3	96	17.7
13	1:1	C/SF	6.5 ± 0.1	3	−5	−3	98	8.7
14	1:3	C/SF	6.8 ± 0.1	4	−4	0	91	9.1
15	3:1	C/SF	6.2 ± 0.1	2	−7	−4	104	8.2
16	1:1	P/SF	8.1 ± 0.1	7	6	3	70	28.5
17	1:3	P/SF	7.1 ± 0.1	4	3	−1	78	18.9
18	3:1	P/SF	9.2 ± 0.1	11	12	9	62	38.6
19	1:1:1	S/C/P	5.4 ± 0.1	5	5	1	99	24.0
20	1:1:1	S/C/SF	5.0 ± 0.1	2	−3	−6	110	10.9
21	1:1:1	S/SF/P	6.7 ± 0.1	5	5	1	91	24.3
22	1:1:1	C/P/SF	7.8 ± 0.1	4	3	−1	83	22.1
23	1:1:1:1	S/C/P/SF	5.7 ± 0.1	3	2	−2	96	20.2

[a] C, CME; P, PME; S, SME; SF, SFME. [b] σ ± 1 (n = 3).

Table 4. Effect of PME on Fuel Properties of SME

	PME/SME vol ratio	OSI (h)	CP[a] (°C)	PP[a] (°C)	CFPP[a] (°C)	IV	SFAME (wt %)
1	0:10[b]	5.0 ± 0.1	1	0	−4	134	14.6
2	1:9	5.2 ± 0.2	2	1	−3	126	17.9
3	2:8	5.4 ± 0.2	4	3	−1	119	21.0
4	3:7	5.6 ± 0.2	5	5	2	111	24.4
5	4:6	5.9 ± 0.3	8	7	4	103	27.3
6	5:5[c]	6.2 ± 0.2	9	8	5	95	30.9
7	6:4	6.9 ± 0.2	11	10	7	87	34.2
8	7:3	7.4 ± 0.2	12	11	8	78	37.9
9	8:2	8.2 ± 0.1	14	13	10	71	40.9
10	9:1	9.2 ± 0.1	15	14	11	63	44.5
11	10:0[b]	10.3 ± 0.1	17	15	12	54	48.2

[a] σ ± 1 (n = 3). [b] From Table 2. [c] From Table 3.

Acid value (AV, mg of KOH g^{-1}) titrations were performed as described in American Oil Chemists' Society (AOCS) official method Cd 3d-63[20] using a Metrohm (Westbury, NY) 836 Titrando autotitrator equipped with a model 801 stirrer, a model 6.0229.100 Solvotrode, and Tiamo 1.1 Light software. The official method was modified for scale to use 2 g of sample and 0.02 M KOH. The titration end point was determined by the instrument and visually verified using a phenolphthalein indicator. Each sample was run

in triplicate (Table 2). The iodine value [IV, g of I_2 (g of sample)$^{-1}$] was calculated from the average fatty ester profile (run in triplicate) of each sample according to the equation found in ref 21 (Tables 2−4).

2.7. Experimental Design. The following mixtures of CME, PME, SME, and SFME were created: binary (1:1, 1:3, and 3:1 by volume), ternary (1:1:1), and quaternary (1:1:1:1). Because SME was unsatisfactory with regard to IV and EN 14112 (OSI) specifications in EN 14214, an additional series of binary mixtures were prepared, in which PME was blended with SME at 10% increments from 10 to 90%. For each blend (n = 31), the following properties were measured: OSI, CP, PP, and CFPP. Furthermore, IV and SFAME content were determined from the fatty ester profile of each blend. Kinematic viscosity (40 °C) and AV were not determined in the case of the blends because CME, PME, SME, and SFME were found to satisfy ASTM D6751 and EN 14214 specifications with regard to these properties. Wear scar lengths by HFRR were not measured for the blends, because all FAME in the neat form exhibited excellent lubricity behavior.

2.8. Statistical Analysis. Data for OSI, IV, CFPP, and total saturated FAME content (SFAME = C12:0 + C14:0 + C16:0 + C18:0 + C20:0 + C22:0) for all samples were imported into SAS for Windows version 9.1 software (SAS Institute, Inc., Cary, NC) for statistical regression analysis. The PROC REG procedure was used to calculate the correlation of determination (R^2), y intercept, slope, degrees of freedom,[33] and p value for each analysis. The PROC CORR procedure was used to determine the Pearson correlation coefficient (PCC) for each analysis.

3. Results and Discussion

3.1. Quality and Properties of Biodiesel Samples. All methyl esters (CME, PME, SME, SFME) were prepared via the classic transesterification procedure, in which sodium methoxide was used as catalyst (0.50 wt % with respect to TAG) in the presence of methanol (mole ratio of 6:1 with respect to TAG) at 60 °C for 1.5 h.[22] Analysis by GC revealed that each sample was free of mono-, di-, and triacylglycerol content (results not shown). Quality was further verified through AV determination, in which all samples were found to be within prescribed ASTM D6751 and EN 14214 specifications [<0.50 mg of KOH (g of sample)$^{-1}$, Table 2].

Methyl oleate was the primary fatty ester in SFME (82.0 wt %) and CME (64.3%), and PME (41.2%) and SME (24.1%) also contained a significant amount. Methyl palmitate (41.9%) was in highest abundance in PME, and methyl linoleate (53.6%) was the most common methyl ester in SME. As expected, unsaturated FAME content was very high in CME (92.3%), SME (85.4%), and SFME (91.2%). Also expected, PME only contained 51.8% unsaturated methyl esters (Table 1). Because of the methyl linoleate content of SME, it displayed the highest

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IV (134, Table 2), which was in excess of the maximum value specified in EN 14214 [120 g of I_2 (g of sample)$^{-1}$]. ASTM D6751 has no IV requirement. All other methyl esters satisfied the EN 14214 specification for IV, with PME exhibiting the lowest value (54). The fatty ester profile and IV data of CME, PME, SME, and SFME are in agreement with results previously reported.[23,24] The total tocopherol content (ppm, Table 1) of CME (766), SME (757), and SFME (655) was considerably higher than that for PME (174), which is also in accordance with previous studies.[24] γ-Tocopherol was in highest abundance in CME (420) and SME (537), whereas α-tocopherol dominated in SFME (497) and PME (122).

The low-temperature fluidity of methyl esters was established by CP, PP, and CFPP determination. In general, the order of cold-flow operability was as follows: CME (best) > SME > SFME > PME (highest CP, PP, and CFPP values, Table 2), which was roughly found to inversely follow saturated FAME content: PME (48.2%) > SME (14.6%) > SFME (9.8%) > CME (7.7%). The trend for oxidative stability, as measured by OSI (EN 14112), was found to be PME (best) > CME ~ SFME > SME (lowest OSI value, Table 2). All samples, with the exception of SME (5.0 h), were satisfactory with respect to the oxidative stability specification in EN 14214 (OSI > 6 h, EN 14112). SME was satisfactory according to the ASTM D6751 requirement (OSI > 3 h, EN 14112). The lower oxidative stability of SME in comparison to the other methyl esters was due to the disproportionately high polyunsaturated FAME content of SME. Polyunsaturated FAME undergo oxidative degradation at significantly faster rates than monounsaturated or saturated methyl esters. For instance, the relative rates of oxidation of the unsaturates were determined to be 1 for oleates, 41 for linoleates, and 98 for linolenates.[25] The kinematic viscosities (40 °C) of all methyl esters were within ASTM D6751 and EN 14214 specifications (Table 2) and yielded the following trend: SME < CME < PME < SFME (highest viscosity). This result is somewhat surprising because saturated methyl esters, of which PME had the greatest amount, are known to be more viscous than unsaturated methyl esters.[8,26] Lastly, all methyl esters displayed excellent lubricity, as evidenced by short wear scar lengths (<200 μm) as determined by HFRR, which is in agreement with previous studies.[1,2,8] Lubricity is not specified in ASTM D6751 and EN 14214 because BD possesses inherently good lubricity. For comparison, ULSD provided wear scar lengths by HFRR in excess of 550 μm in the absence of proprietary lubricity-enhancing additives,[27] which is beyond the maximum wear scar lengths allowed in petrodiesel standards, such as ASTM D975[28] (<520 μm) and EN 590[29] (<460 μm).

3.2. Improvement of OSI and IV of SME. In a previous study, the OSI of jatropha oil methyl esters (JME) was improved through blending with PME.[11] A similar approach was under-

taken in the current study to improve the IV and OSI of SME. The IV of SME was reduced to an acceptable level according to EN 14214 (<120) through blending with PME at nearly any ratio investigated (entries 4−6, Table 3; entries 3−10, Table 4). The only ratio of PME in SME that did not yield an IV of less than 120 was 1:9 (entry 2, Table 4). Both CME and SFME were successful in lowering the IV of SME to less than 120, as evidenced by entries 2, 7, and 8 of Table 3. However, CME and SFME were less effective than PME in lowering the IV of SME because of the higher saturated FAME content and lower polyunsaturated FAME content of PME in comparison to CME and SFME (Table 1). Comparison of blends in which the ratio of SME to other BD was 1:3 is illustrative of the relative effectiveness of CME (IV 116, entry 2, Table 3), SFME (IV 97, entry 8, Table 3), and PME (IV 73, entry 5, Table 3) at reducing the IV of SME. All ternary and quaternary mixtures that contained SME provided IV values that were satisfactory according to EN 14214 (entries 19−21 and 23, Table 3).

The oxidative stability of SME was improved to an acceptable level according to EN 14214 (OSI > 6 h, EN 14112) through blending with PME at ratios in which the PME content was equal to or greater than 50% (entries 4 and 5, Table 3; entries 6−10, Table 4). In general, the OSI of SME was improved in a linear fashion with increasing PME content. Blending of SFME with SME also afforded OSI > 6 h (entry 8, Table 3). On the basis of the results of Table 3 (entries 1−3), the CME content in a binary mixture with SME must be greater than 75% to provide OSI values in excess of 6 h. Of the ternary and quaternary mixtures containing SME, the only mixture that was found to be satisfactory was that of SME, SFME, and PME (1:1:1, entry 21, Table 3). The improvement in OSI of SME through blending was attributed to the reduction in polyunsaturated FAME content of the blends in comparison to neat SME. All blends in this study were satisfactory according to the oxidative stability specification in ASTM D6751 (OSI > 3 h, EN 14112). These results are in agreement with a previous study, which indicated that the OSI of SME could be improved through blending with rapeseed oil methyl esters (RME) and PME.[9]

3.3. Improvement of CFPP of PME. Low-temperature operability is an important factor that must be considered when operating compression-ignition engines (diesel) in moderate temperature climates during winter months. Once the CFPP is reached, the fuel will contain solids of sufficient size to render the engine inoperable because of fuel filter plugging.[1,2,8,9,30,31] Therefore, it is advantageous to use fuels with CFPP values that are as low as possible. In the case of PME, CFPP is poor (12 °C, Table 2); however, CFPP values at or less than 0 °C were obtained through blending with other methyl esters. For instance, 25% PME in CME, SME, and SFME yielded CFPP ≤ 0 °C (entries 12, 6, and 17, respectively, Table 3). Furthermore, 10 and 20% PME in SME provided CFPP < 0 °C (entries 2 and 3, Table 4). Lastly, the ternary mixture of CME, PME, and SFME (1:1:1) and the quaternary mixture (1:1:1:1) afforded CFPP < 0 °C (entries 22 and 23, respectively, Table 3). In general, binary mixtures in which PME was present at 25% or less yielded CFPP values ≤0 °C. These results are in agreement with a previous study, which indicated that the CFPP of PME could be improved through blending with RME and

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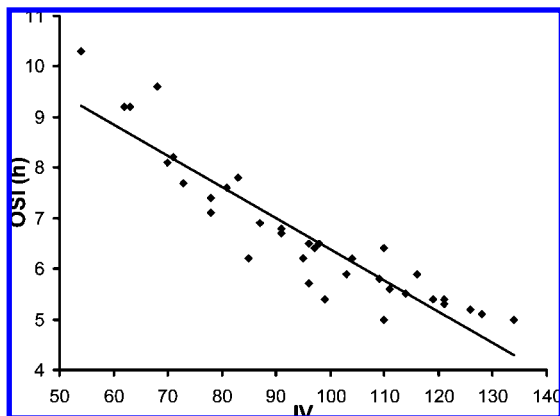
Figure 1. Relationship between OSI and IV; $R^2 = 0.848$; y intercept $= 12.561$; slope $= -0.062$; PCC $= -0.921$; p value $= <0.0001$.
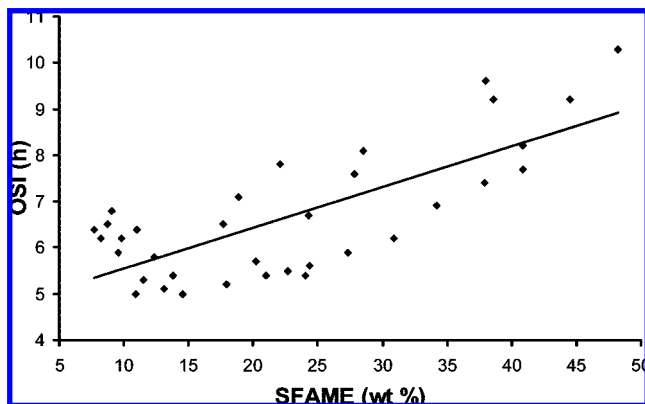
Figure 2. Relationship between OSI and SFAME content; $R^2 = 0.561$; y intercept $= 4.669$; slope $= 0.088$; PCC $= 0.749$; p value $= <0.0001$.

SME.[9] Additionally, the CFPP of PME was improved by 7 °C in a prior study through employment of a 60% mixture of JME in PME.[11]

3.4. Relationship of OSI to IV, SFAME, and CFPP. Relationships between fuel properties were considered statistically significant if the absolute values of the Pearson correlation coefficients (PCC) for 33 degrees of freedom were greater than 0.449 for p values <0.01.[32] According to this parametric, statistically significant relationships were elucidated between OSI and IV (Figure 1), OSI and SFAME content (Figure 2), and OSI and CFPP (Figure 3). In the case of OSI versus IV (Figure 1), an inverse relationship (PCC -0.921) was found, in which 84.8% of the change in OSI was attributed to IV ($R^2 = 0.848$). Although this represents a statistically significant relationship, other important factors besides IV may influence OSI, such as differences in native antioxidant content (tocopherols, tocotrienols, phytosterols, etc.) across different samples of similar IV, differing sample histories (differences in exposure to elevated temperature, UV irradiation, oxygen, extended storage, etc.), and differences in fatty acid content (a prooxidant). Furthermore, a great many fatty ester compositions are possible for a given IV, which may result in dissimilar OSI values. For instance, examination of the data contained in Tables 2−4 reveals that four samples have an IV at or near 110 (CME, Table 2; entries 7 and 20, Table 3; entry 4, Table 4). However, the OSI values for these samples (IV 110 ± 1) were 6.4, 5.8, 5.0, and 5.6 h, respectively. Another illustrative example is that of entries 13 and 19 of Table 3, which had IV values of 98−99;
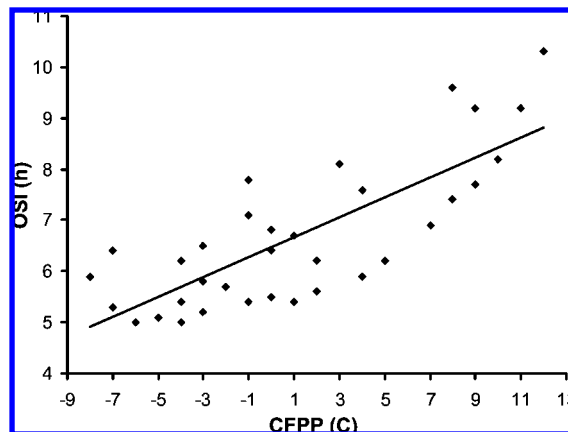
Figure 3. Relationship between OSI and CFPP; $R^2 = 0.611$; y intercept $= 6.473$; slope $= 0.191$; PCC $= 0.781$; p value $= <0.0001$.

however, the OSI values for these samples were 6.5 and 5.4 h. Therefore, although a statistically significant relationship was discovered between OSI and IV, it is of limited practical value. This conclusion is supported by a previous study that questions the utility of IV as a predictor of oxidative stability.[21]

In the case of OSI versus SFAME content (Figure 2), a direct relationship (PCC 0.749) was discovered, in which 56.1% of the change in OSI was attributed to SFAME content ($R^2 = 0.561$). Although this represents a statistically significant relationship, other important factors besides SFAME content may influence OSI, such as differences in native antioxidant content among samples, storage history, fatty acid content, and the type of unsaturates present in samples of similar SFAME content. As mentioned previously, trienoic FAME undergo oxidation at considerably faster rates than di- or monoenoic FAME.[25] For example, entries 8 and 20 of Table 3 had similar SFAME content (∼11 wt %) but significantly different OSI values (6.4 and 5.0 h, respectively). Another example is entries 6 and 22 (22.7 and 22.1 wt %, respectively, Table 3), which exhibited OSI values of 5.5 and 7.8 h. Yet another example is that of SME (SFAME content 14.6%, Table 1; OSI 5.0 h, Table 2) in comparison to entries 2, 13, 14, and 15 of Table 3 and neat CME and SFME, which had lower SFAME content than SME but higher OSI values. Therefore, although a statistically significant relationship was discovered between OSI and SFAME content, it is of limited practical value.

In the case of OSI versus CFPP (Figure 3), a direct relationship (PCC 0.781) was found, in which 61.1% of the change in OSI was attributed to CFPP ($R^2 = 0.611$). Although this represents a statistically significant relationship, other important factors besides CFPP may influence OSI, such as fatty ester composition, fatty acid content, native antioxidant content, and storage history. For example, samples with CFPP of 8 °C (entry 11, Table 3; entry 8, Table 4) had OSI values of 9.6 and 7.4 h, respectively. Another example is that of samples with CFPP of -1 °C (entries 17 and 22, Table 3; entry 3, Table 4), which exhibited OSI values of 7.1, 7.8, and 5.4 h, respectively. Therefore, although a statistically significant relationship was uncovered between OSI and CFPP, it is of limited practical value.

3.5. Dependence of CFPP on IV and SFAME Content. Statistically significant relationships were discovered between CFPP and IV (Figure 4) and SFAME content (Figure 5). In the case of CFPP versus IV (Figure 4), an inverse relationship (PCC
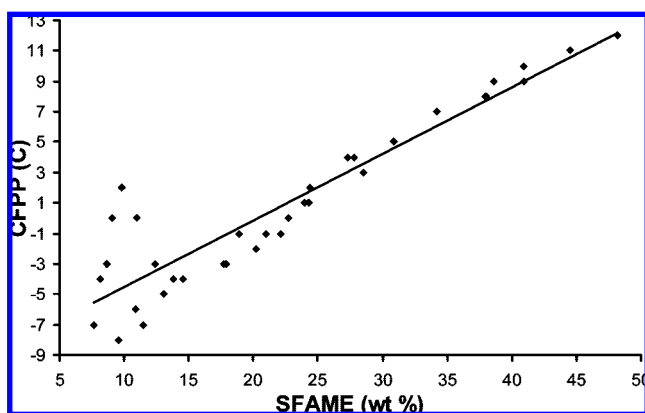
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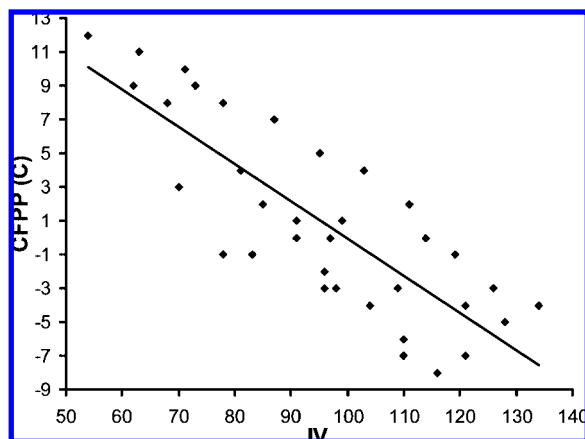
Figure 4. Relationship between CFPP and IV; $R^2 = 0.674$; y intercept $= 22.031$; slope $= -0.221$; PCC $= -0.821$; p value $= <0.0001$.

Figure 5. Relationship between CFPP and SFAME content; $R^2 = 0.861$; y intercept $= -8.930$; slope $= 0.438$; PCC $= 0.928$; p value $= <0.0001$.

-0.821) was found, in which 67.4% of the change in CFPP was attributed to IV ($R^2 = 0.674$). Although this represents a statistically significant relationship, other important factors besides IV may influence CFPP, such as the presence of minor components (sterol glucosides, mono-, di-, and triacylglycerols, etc.) and variable fatty ester compositions for samples of similar IV. For instance, samples that had an IV value at or near 110 (CME, Table 2; entries 7 and 20, Table 3; entry 4, Table 4) yielded CFPP values of -7, -3, -6, and 2 °C, respectively. Another example is that of entries 13 and 19 of Table 3, which had IV values of 98–99; however, the CFPP values for these

samples were -3 and 1 °C, respectively. Therefore, although a statistically significant relationship was discovered between CFPP and IV, it is of limited practical value.

In the case of CFPP versus SFAME content (Figure 5), a direct relationship (PCC 0.928) was found, in which 86.1% of the change in CFPP was attributed to SFAME content ($R^2 = 0.861$). Although this represents a statistically significant relationship, other factors besides SFAME content may influence CFPP, such as the presence of minor components and the nature of unsaturated FAME in samples of similar SFAME content. For example, entries 8 and 20 of Table 3 had similar SFAME content ($\sim$11 wt %) but different CFPP values (0 and -6 °C, respectively). As can be seen from examination of Figure 5, samples with SFAME content <12 wt % had widely varying CFPP values but samples with SFAME content >12 wt % displayed a nearly linear relationship between CFPP and SFAME. In fact, a R^2 of 0.0011 was obtained for samples with SFAME < 12 wt %, which is decidedly not a statistically significant relationship. For samples with SFAME content >12 wt %, a R^2 value of 0.978 was obtained (PCC 0.989), which is a very strong statistically significant relationship. Therefore, a strong statistical and practical relationship exists between CFPP and SFAME content for samples with SFAME content greater than 12 wt %. For samples with SFAME content less than 12 wt %, no statistically significant relationship was found between CFPP and SFAME content.

4. Conclusions

The following conclusions were elucidated from the results discussed above: (1) The IV and OSI of SME was improved to satisfy EN 14214 specifications through blending with CME, PME, or SFME. (2) The CFPP of PME was improved through blending with CME, SME, and SFME. (3) Statistically significant relationships were discovered between OSI and IV, OSI and SFAME content, OSI and CFPP, CFPP and IV, and CFPP and SFAME content. (4) The only statistically significant relationship that was of practical significance was that of CFPP versus SFAME content when SFAME content was greater than 12 wt %. (5) Fuel properties of BD can be significantly modified through blending with BD obtained from different feedstocks.